



# Combinatorial Measurement of Polymer Craze Growth and Fracture

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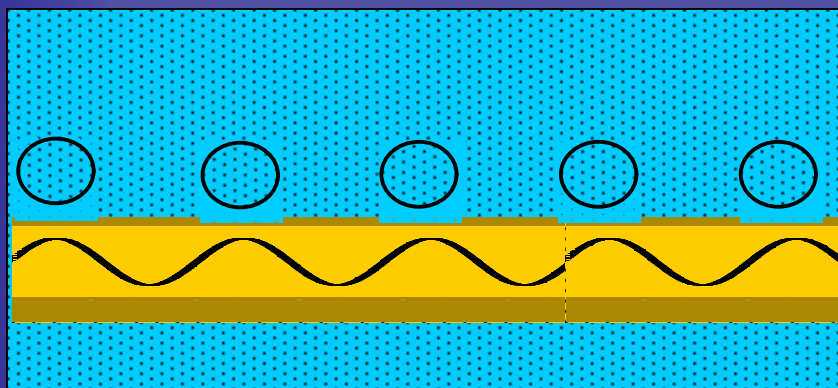
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Materials Science and Engineering Laboratory  
Polymers Division  
Gaithersburg, MD



# Craze Growth and Fracture in Thin Films

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- Toughness of polymer related to craze formation
- Decades of research history on crazing
- Heterogeneities in processing of thin films may play role in craze formation and fracture properties



Craze Fibrils (behind craze front)

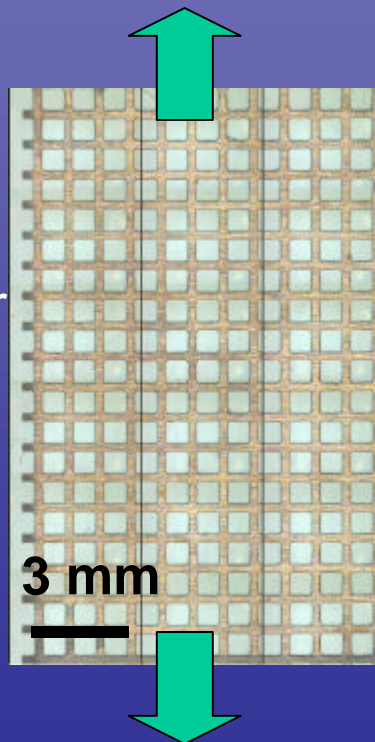
Craze Front (Taylor Instability)



# The Copper Grid Test

- Lauterwasser, B.D. and E.J. Kramer. “Microscopic mechanisms and mechanics of craze growth and fracture”, *Phil. Mag. A*, **39**, 4, 469-495, 1979.

Copper Grid  
coated with  
glassy polymer



- Isolate crazes in thin films
- Statistical population of equally strained cells in one sample
- Copper plastically deforms to “lock-in” applied strain
- Use microscopy to analyze craze and fracture microstructures



# Combinatorial Approach to Polymer Thin Films (gradients)

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## *Variables:*

- Film thickness
- Crosslink density
- Chemical functionality
- Crystallinity
- Blend composition
- Surface Patterns

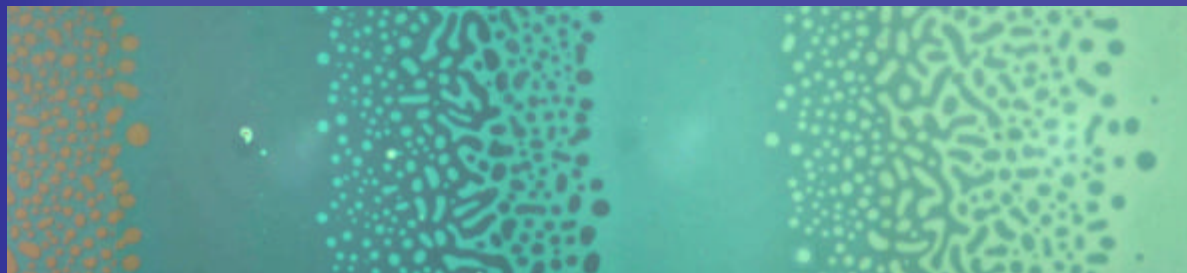
## *Properties:*

- Confinement
- Surface energy
- Adhesion energy
- Toughness
- Biocompatibility
- Miscibility /  
Phase separation
- Wettability

Polystyrene →  
H ~ 40 -120 nm



Poly(styrene-*b*-methyl methacrylate)  
H ~ 40 -120 nm →



Poly(vinyl cinnamate)  
H ~ 120 nm



UV →

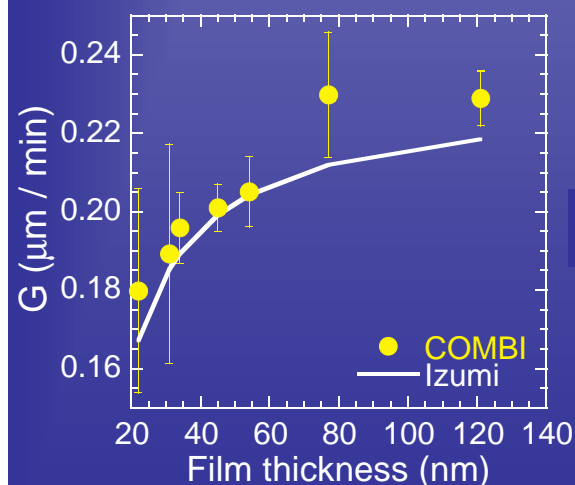
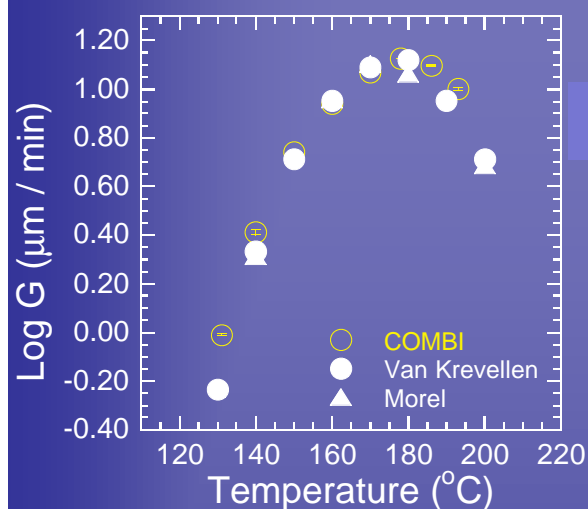




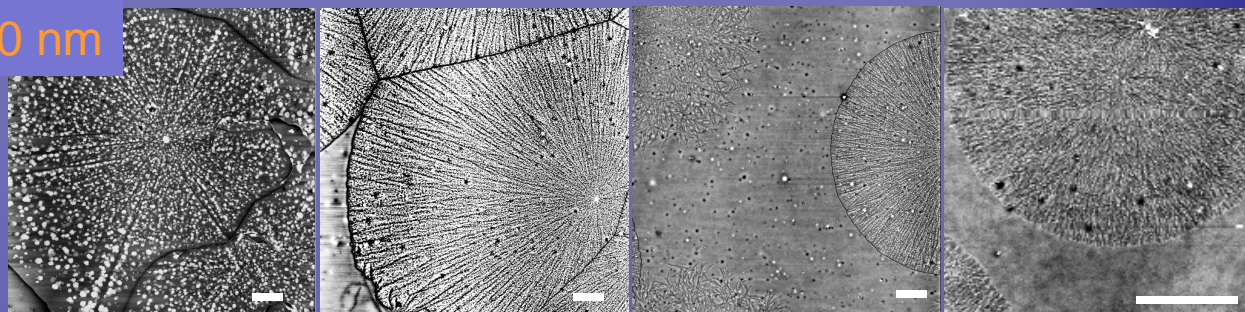
# Craze Growth in Semi-Crystalline Thin Films: ipS

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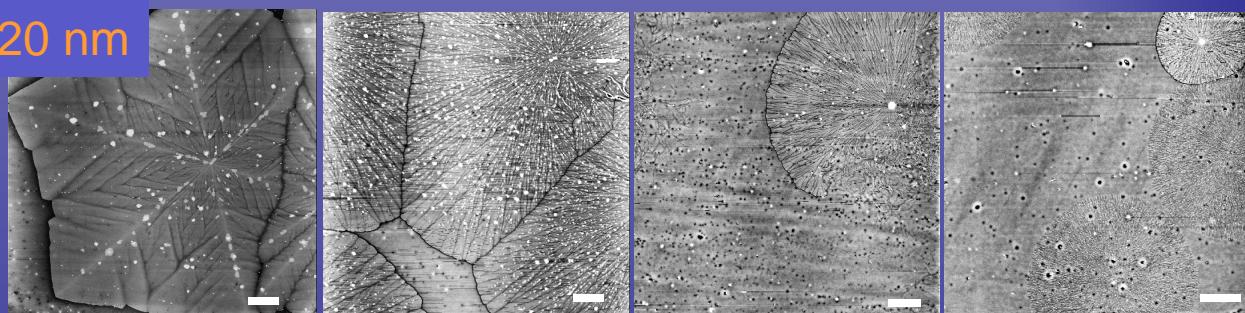
Gradients in film thickness and temperature lead to gradients in crystal structure and degree of crystallinity.



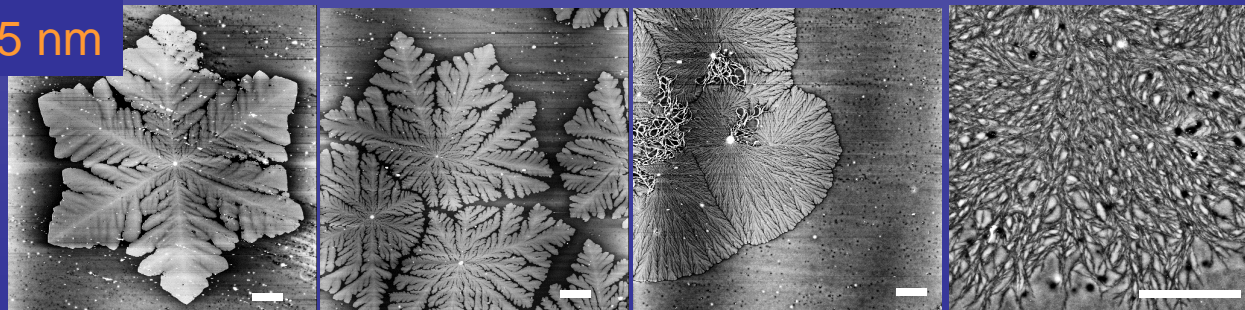
> 30 nm



~ 20 nm



< 15 nm



190 °C

170 °C

150 °C

130 °C

American Physical Society  
Fall Meeting

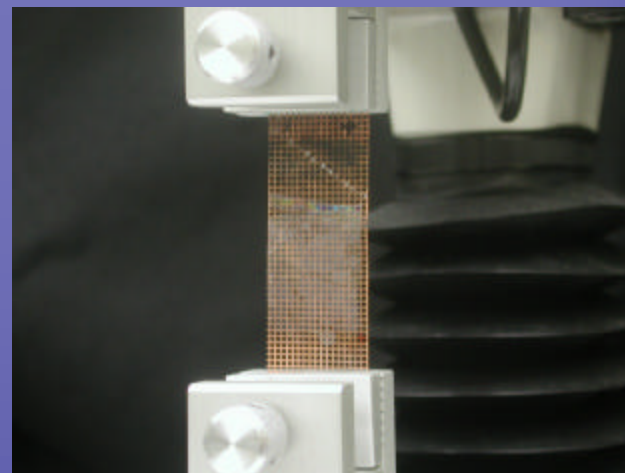
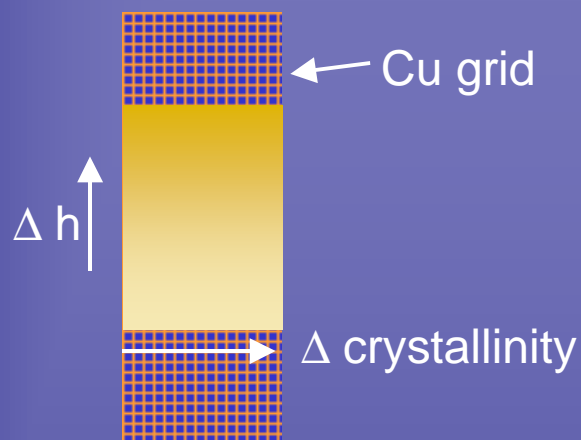
Scale bars: 10 μm

March 18, 2002

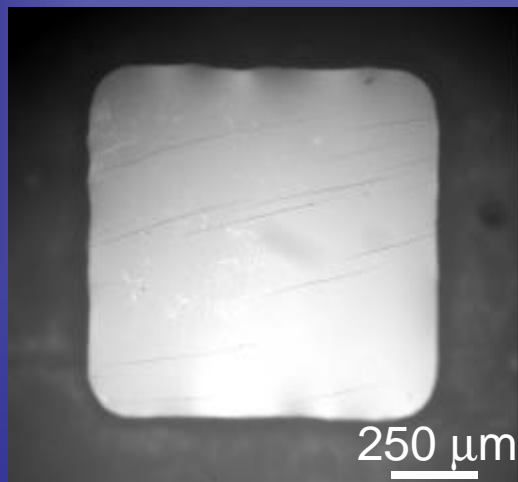


# Combinatorial Approach with the Copper Grid Experiment

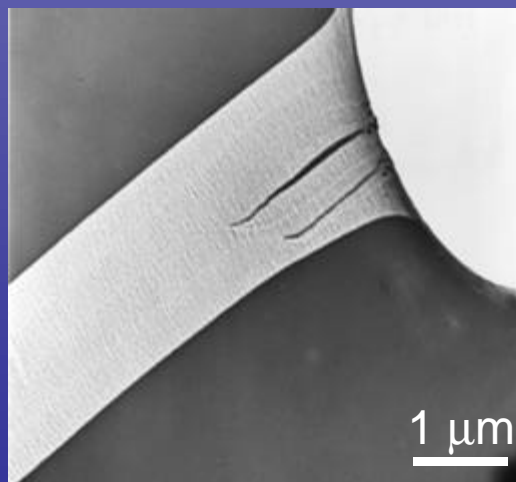
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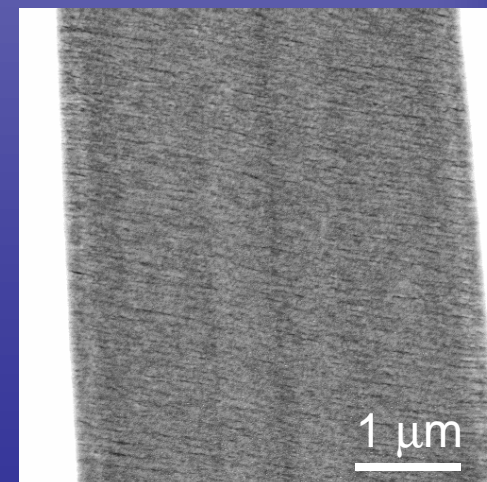
OM



TEM



AFM





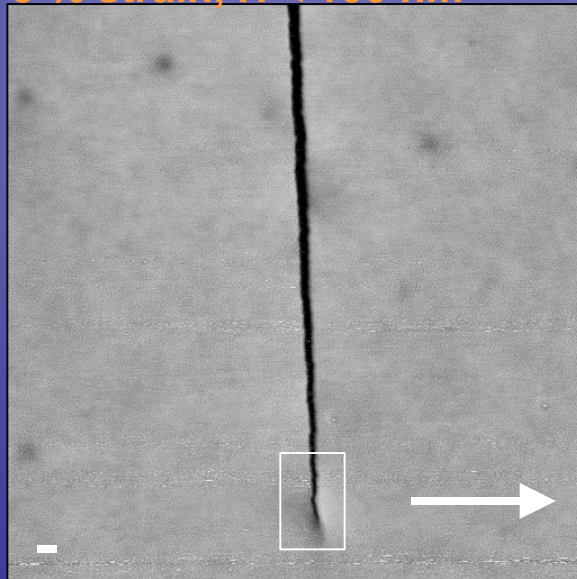


# AFM of Craze Tips

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In the early stages of craze growth, little difference is observed between tip structure in films above and below 100 nm thick.

3 % strain,  $H < 100$  nm

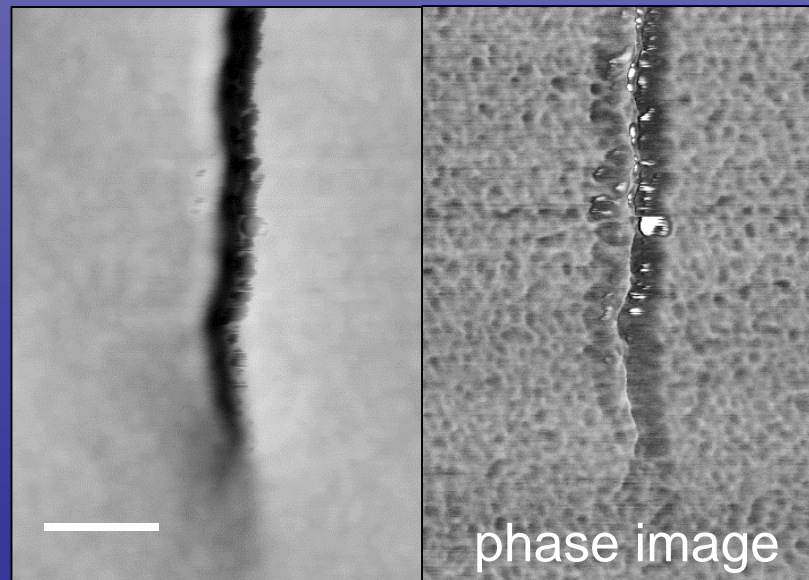


Scale bars: 100 nm

**Tip images:** always into amorphous film, never in contact with any other structures



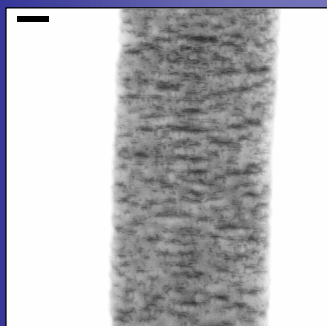
**Mid-Section Images:** Far away from tip and any evidence of change in cross section size





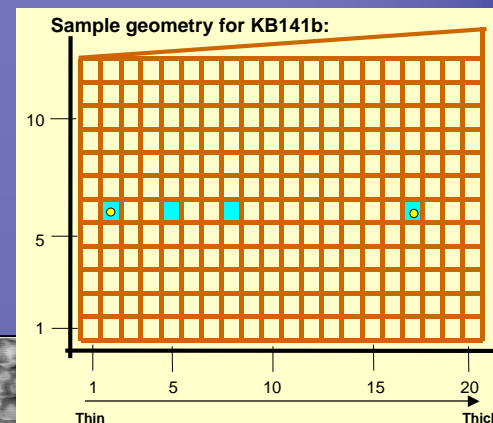
# AFM of Craze Mid-Section

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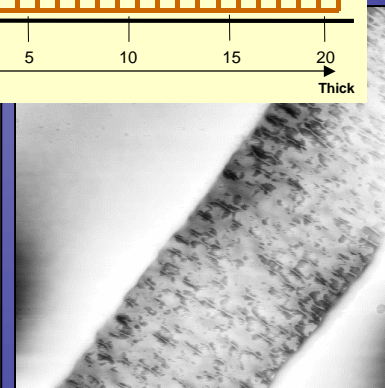
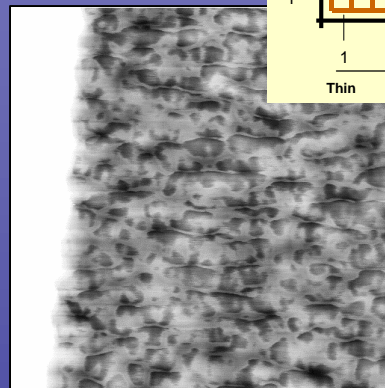
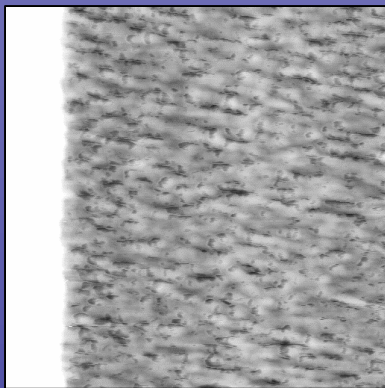
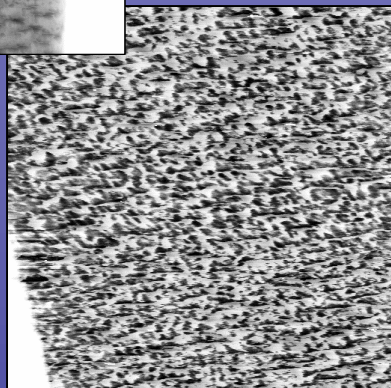


Scale bars: 100 nm

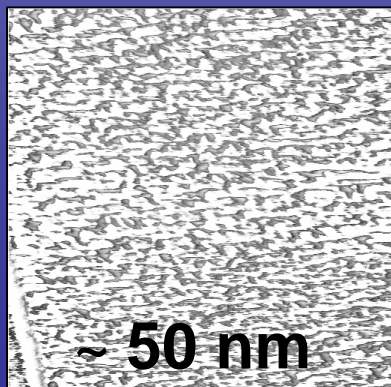
3 % strain



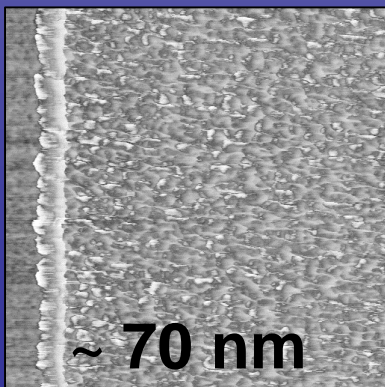
Height



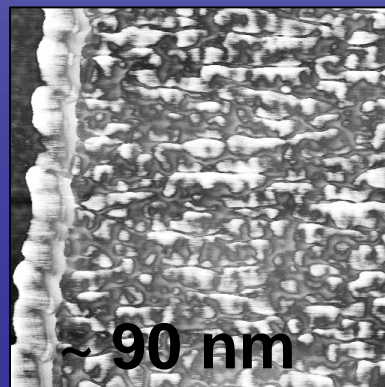
Phase



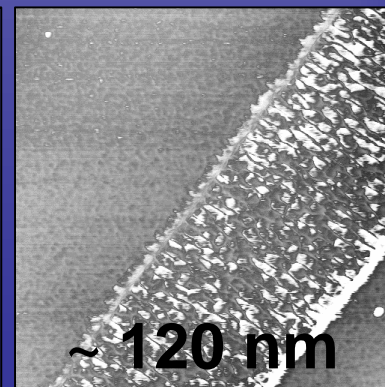
~ 50 nm



~ 70 nm



~ 90 nm



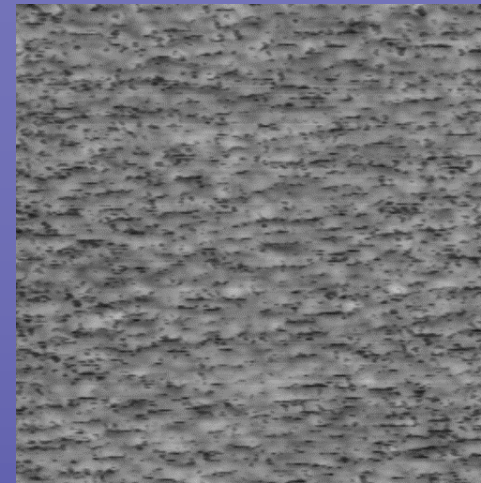
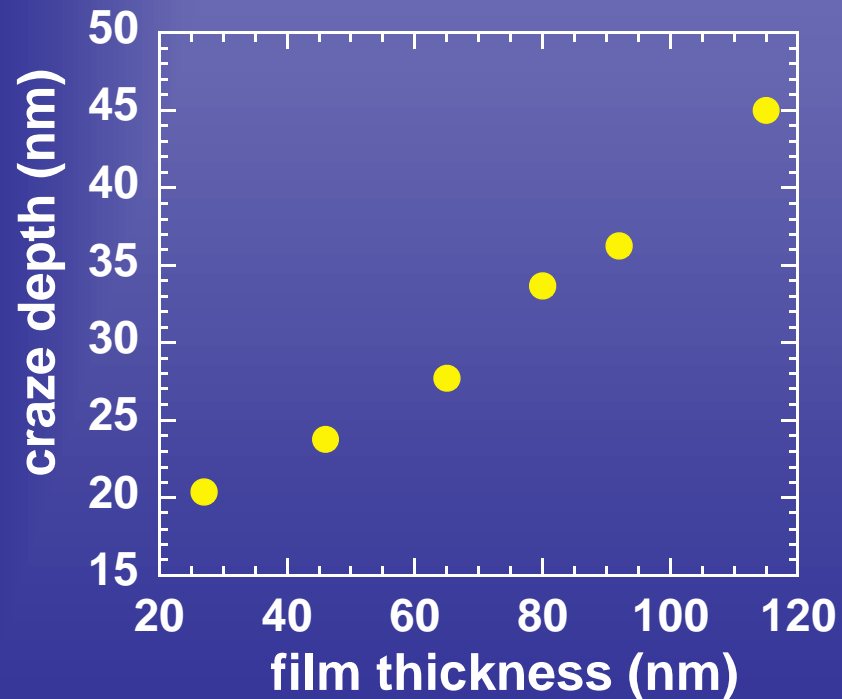
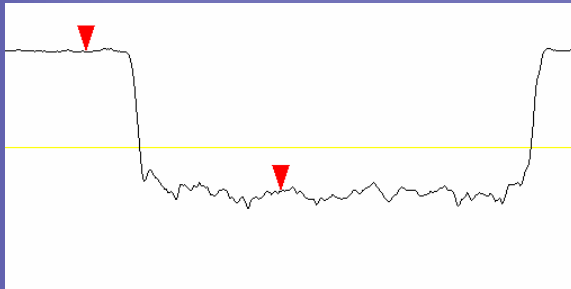
~ 120 nm





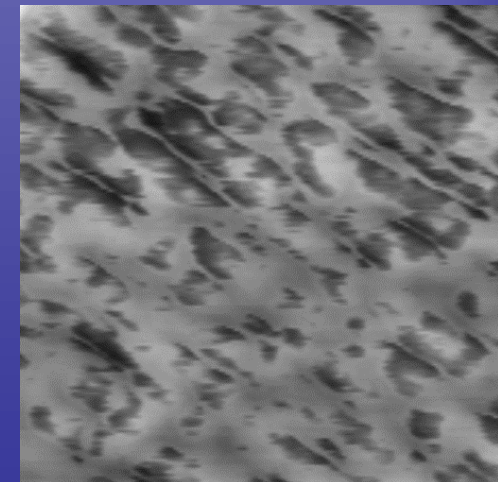
# Craze Depth and Roughness

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3 % strain  
H ~ 50 nm

3 % strain  
H ~ 100 nm





# Conclusions / Future Plans



- Demonstrated applicability of the gradient combinatorial approach and AFM analysis to studying craze growth and fracture in thin films
- Future plans include pre- and post-strain crystallization (second gradient) as well as gradients in crosslink density, and other gradient variables

## Acknowledgments:

Paul Smith  
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